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Partially esterified copolymers of monoethylenically unsaturated dicarboxylic anhydrides, vinylaromatic compounds and further monoethylenically unsaturated monomers containing heteroatoms

The present invention relates to copolymers which are obtainable by free-radical polymerization of

(A) at least one monoethylenically unsaturated C_4-C_8-dicarboxylic anhydride,

(B) at least one vinylaromatic compound from the group consisting of styrene and substituted styrenes and

(C) at least one monoethylenically unsaturated monomer which contains at least one heteroatom and is different from (A),

and partial esterification of the resulting copolymers with

(D) alcohol alkoxylates of the formula I

$$HO\!-\!\left(R\!-\!O\right)_n\!-\!R^1 \qquad \mathrm{I}$$

in which the variables have the following meanings:

R is C_2-C_6-alkylene radicals, which, when n is > 1, may be identical or different;
R^1 is C_1-C_{30}-alkyl;
n is 1 to 200,

and if desired hydrolysis of the anhydride groups still present in the copolymers to give carboxyl groups.

Furthermore, the invention relates to the use of these copolymers as additive for detergents and cleaners, in particular as graying-inhibiting and detergency-boosting additive in detergents, and also to solid and liquid detergents which comprise the copolymers as additive.

In the washing process, a distinction is drawn between primary and secondary detergency. Primary detergency is understood as meaning the actual removal of soiling from the textile ware. Secondary detergency is understood as meaning the prevention of the effects which arise as the result of redeposition of the detached soiling from the wash liquor onto the fabric. The textiles become increasingly gray from washing operation to washing operation and this insidious graying process can scarcely be reversed. In order to protect textiles made of cotton from becoming gray,

sodium salts of carboxymethylcellulose (CMC) are often added to the detergent. Polyacrylic acids and acrylic acid-maleic acid copolymers also have a graying-inhibiting action. However, the action of said polymers is not satisfactory for clay-containing soiling.

EP-A-945 473 and 945 501 describe graft copolymers of styrene, maleic anhydride and polyethylene glycols which are used as soil repellent additive in cleaning formulations and detergents.

US-A-3 485 762 discloses detergent compositions which comprise ammonium salts of a styrene-maleic anhydride copolymer partially esterified with a nonionic surfactant as detergency booster.

Styrene-maleic anhydride copolymers partially esterified with polyethylene glycols are also known from EP-A-306 449, according to which they can be used as cement liquefiers.

It is an object of the present invention to provide polymeric detergent additives which are characterized by overall advantageous application properties, in particular have improved primary and secondary detergency and can be readily and stably incorporated into solid and liquid detergent formulations.

We have found that this object is achieved by copolymers which are obtainable by free-radical polymerization of

(A) at least one monoethylenically unsaturated C_4-C_8-dicarboxylic anhydride,

(B) at least one vinylaromatic compound from the group consisting of styrene and substituted styrenes and

(C) at least one monoethylenically unsaturated monomer which contains at least one heteroatom and is different from (A),

and partial esterification of the resulting copolymers with

(D) alcohol alkoxylates of the formula I

$$HO-\left(-R-O-\right)_n-R^1 \qquad \text{I}$$

in which the variables have the following meanings:

R is C_2-C_6-alkylene radicals, which, when n is > 1, may be identical or different;
R^1 is C_1-C_{30}-alkyl;
n is 1 to 200,

and if desired hydrolysis of the anhydride groups still present in the copolymers to give carboxyl groups.

As a rule, the copolymers according to the invention have the following composition: the molar ratios of (B) to (A) and of (C) to (A) are in each case in the range from 0.1:1 to 10:1, where the molar ratio of [(B) + (C)] to (A) is 20:1 to 1:2.

In this connection, for the molar ratio of (B) to (A), a range from 0.2:1 to 5:1 is preferred, and from 0.3:1 to 3:1 is particularly preferred.

The molar ratio of (C) to (A) is preferably 0.1:1 to 5:1, in particular 0.1:1 to 3:1.

The molar ratio of [(B) + (C)] to (A) is preferably 10:1 to 1:1 and particularly preferably 6:1 to 1:1.

Used as monomer (A) for the preparation of the copolymers according to the invention are monoethylenically unsaturated dicarboxylic anhydrides having 4 to 8 carbon atoms. Examples which may be specifically mentioned are maleic anhydride, itaconic anhydride, citraconic anhydride and methylenemalonic anhydride. Preference is given here to itaconic anhydride and in particular maleic anhydride.

The vinylaromatic monomers (B) used are styrene and substituted styrenes, such as alkylstyrenes, in particular C_1-C_4-alkylstyrenes, e.g. methylstyrenes and ethylstyrenes, styrenesulfonic acids and salts thereof and halogenated styrenes, in particular chlorostyrenes, very particular preference being given to unsubstituted styrene.

Suitable as monomer (C) are a number of monoethylenically unsaturated compounds having at least one heteroatom. The heteroatoms, e.g. nitrogen or oxygen atom, can be incorporated into the carbon chain or be present in the form of a functional group, e.g. a carboxyl, ester, amide or cyano group.

Examples of particularly suitable monomers (C) which may be mentioned are:

- monoethylenically unsaturated C_3-C_5-carboxylic acids, such as maleic acid, fumaric acid, crotonic acid and in particular acrylic acid and methacrylic acid;

- C_1-C_{22}-alkyl esters of monoethylenically unsaturated C_3-C_5-carboxylic acids, in particular (meth)acrylic esters, such as methyl, ethyl, propyl, n-butyl, isobutyl,

2-ethylhexyl, decyl, lauryl, isobornyl, cetyl, palmityl and stearyl (meth)acrylate, basic esters of these carboxylic acids, in particular dialkylaminoalkyl (meth)acrylates, such as dimethylaminoethyl and diethylaminoethyl (meth)acrylate and dimethylaminopropyl and diethylaminopropyl (meth)acrylate, and salts thereof, and esters with methylpolyalkylene glycols, such as methylpolyethylene glycol (meth)acrylates with an average molecular weight M_n of from 200 to 5 000;

- (meth)acrylamides, such as (meth)acrylamide, N-(C_1-C_{12}-alkyl)- and N,N-di(C_1-C_4-alkyl)(meth)acrylamides, such as N-methyl-, N,N-dimethyl-, N-ethyl-, N-propyl-, N-tert-butyl-, N-tert-octyl- and N-undecyl(meth)acrylamide, ethoxylation products thereof, such as methylpolyethylene glycol (meth)acrylamides with an average molecular weight M_n of from 200 to 5 000, and basic amides of these carboxylic acids, in particular N,N-(di-C_1-C_3-alkyl)amino-C_2-C_6-alkyl(meth)acrylamides, such as dimethylaminoethyl- and diethylaminoethyl(meth)acrylamide and dimethylaminopropyl- and diethylaminopropyl(meth)acrylamide;

- vinyl esters of C_2-C_{30}-carboxylic acids, in particular C_2-C_{14}-carboxylic acids, such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl 2-ethylhexanoate and vinyl laurate;

- vinyl C_1-C_{30}-alkyl ethers, in particular vinyl C_1-C_{18}-alkyl ethers, such as vinyl methyl ether, vinyl ethyl ether, vinyl n-propyl ether, vinyl isopropyl ether, vinyl n-butyl ether, vinyl isobutyl ether, vinyl 2-ethylhexyl ether and vinyl octadecyl ether;

- N-vinylamides and N-vinyllactams, such as N-vinylformamide, N-vinyl-N-methylformamide, N-vinylacetamide, N-vinyl-N-methylacetamide, N-vinylpyrrolidone, N-vinylpiperidone and N-vinylcaprolactam;

- allyl alcohol alkoxylates of the formula $H\text{-}(O\text{-}R')_m\text{-}O\text{-}CH_2\text{-}CH{=}CH_2$ (R': linear or branched C_2-C_7-alkylene, preferably ethylene or propylene; m: 1 to 500, preferably 2 to 300);

- vinyl-substituted nitrogen heterocycles, such as 1-vinylimidazole, 2-methyl-1-vinylimidazole, N-vinyloxazolidone, N-vinyltriazole, 2-vinylpyridine, 4-vinylpyridine, 4-vinylpyridine N-oxide, N-vinylimidazoline and N-vinyl-2-methylimidazoline;

- nitriles, such as acrylonitrile and methacrylonitrile.

Preferred monomers (C) are acrylic acid, methacrylic acid, (meth)acrylic esters and amides, in particular methyl acrylate, methyl methacrylate and acrylamide, vinyl alkyl ethers, in particular vinyl n-butyl ether and vinyl isobutyl ether, N-vinylamides, in

particular N-vinylformamide and N-vinylpyrrolidone, and vinyl-substituted nitrogen heterocycles, in particular 1-vinylimidazole and 4-vinylpyridine.

The esterification component (D) used are alcohol alkoxylates of the formula I

$$HO\left(R-O\right)_n R^1 \qquad I$$

Here, R is linear or branched C_2-C_6-alkylene, preferably ethylene, propylene or butylene. The radicals R can, when n is > 1, be identical or different. Different radicals R may be arranged blockwise or randomly.

R^1 is linear or branched C_1-C_{30}-alkyl.

Finally, n is 1 to 200, preferably 4 to 100, particularly preferably 4 to 50.

Examples of particularly suitable components (D) are:

- polyethylene glycols of the formula I capped at one end with methyl end groups and in which n is 1 to 200, preferably 4 to 100 and particularly preferably 4 to 50;
- block copolymers of ethylene oxide, propylene oxide and/or butylene oxide capped at one end with methyl end groups and having an average molecular weight M_n of from 300 to 5 000;
- random copolymers of ethylene oxide, propylene oxide and/or butylene oxide capped at one end with methyl end groups and having a molecular weight M_n of from 300 to 5 000;
- alkoxylated C_2-C_{30}-alcohols, in particular fatty alcohol alkoxylates, oxo alcohol alkoxylates or Guerbet alcohol alkoxylates, where the alkoxylation can be carried out with ethylene oxide, propylene oxide and/or butylene oxide, e.g.

  $C_{13}C_{15}$-oxo alcohol ethoxylates with 3 to 30 ethylene oxide units,
  C_{13}-oxo alcohol ethoxylates with 3 to 30 ethylene oxide units,
  $C_{12}C_{14}$-fatty alcohol ethoxylates with 3 to 30 ethylene oxide units,
  C_{10}-oxo alcohol ethoxylates with 3 to 30 ethylene oxide units,
  C_{10}-Guerbet alcohol ethoxylates with 3 to 30 ethylene oxide units,
  C_9C_{11}-oxo alcohol alkoxylates with 2 to 20 ethylene oxide units, 2 to 20 propylene oxide units and/or 1 to 5 butylene oxide units,
  $C_{13}C_{15}$-oxo alcohol alkoxylates with 2 to 20 ethylene oxide units, 2 to 20 propylene oxide units and/or 1 to 5 butylene oxide units,

C_4C_8-alcohol ethoxylates with 2 to 20 ethylene oxide units.

The copolymers according to the invention are partially esterified with the alcohol alkoxylates I. In general, 5 to 80%, preferably 10 to 65%, particularly preferably 20 to 50%, of the carboxyl groups present are esterified.

Preferably, the copolymers according to the invention do not contain anhydride groups, i.e. unesterified anhydride groups are hydrolyzed to carboxyl groups. The hydrolysis can be carried out with water or in particular with aqueous bases, as a result of which the carboxyl groups are converted to the corresponding salts.

The K values of the copolymers according to the invention are usually 6 to 200, in particular 10 to 100 (measured in accordance with H. Fikentscher at 25°C in water and a polymer concentration of 1% by weight).

The preparation of the copolymers according to the invention can take place by solution polymerization, suspension polymerization or solvent-free by bulk polymerization of the monomers (A), (B) and (C) and subsequent partial esterification with (D), and, if desired, hydrolysis.

Suitable solvents here are polar solvents which are inert toward the acid anhydrides (A), e.g. acetone, tetrahydrofuran or dioxane. Suitable precipitating agents are, for example, toluene, xylene or aliphatic hydrocarbons.

The polymerization generally takes place at temperatures of from 40 to 200°C, preferably 60 to 150°C, over the course of 0.5 to 12 h, preferably 1 to 8 h and particularly preferably 1 to 5 h.

The polymerization is triggered in all of the processes using polymerization initiators. Suitable polymerization initiators here are all compounds which decompose into free radicals, e.g. peroxides, hydroperoxides, redox initiators and azo compounds, such as di-tert-butyl peroxide, tert-butyl peroctoate, tert-butyl perpivalate, tert-butyl per-2-ethylhexanoate, tert-butyl permaleate, tert-butyl perisobutyrate, benzoyl peroxide, diacetyl peroxide, succinyl peroxide, p-chlorobenzoyl peroxide, dicyclohexyl peroxide dicarbonate, 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-methylpropion-amidine) dihydrochloride and 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile). In general, these initiators are used in amounts of from 0.1 to 20% by weight, preferably 0.2 to 15% by weight, based on the weight of the monomers (A), (B) and (C).

The esterification of the copolymers with the alcohol alkoxylate (D) can be carried out in inert solvents or swelling agents, such as acetone, methyl ketone, tetrahydrofuran, toluene, xylene or aliphatic hydrocarbons, or in bulk. The amount of (D) is chosen here

such that only partial esterification of the copolymers arises. The esterification can be accelerated by adding catalysts, in particular acidic catalysts, such as sulfuric acid, methanesulfonic acid, p-toluenesulfonic acid, dodecylbenzenesulfonic acid, hydrochloric acid or acidic ion exchangers. Following the esterification, the solvents, where used, are removed from the reaction mixture. If required, the partially esterified copolymers obtained are dissolved in water with the addition of bases. As a result, anhydride groups which are still present are hydrolyzed and converted to carboxylate groups. Suitable bases are, for example, sodium hydroxide solution, potassium hydroxide solution, ammonia, amines and alkanolamines. The pH of the copolymer solutions obtained in this way is generally 3 to 10 and preferably 5 to 8.

It is particularly advantageous for the alcohol alkoxylate (D) itself to be used as solvent or diluent for the copolymerization of (A), (B) and (C). When the copolymerization is complete, the reaction with (D) can be started or completed by increasing the temperature and/or adding catalysts. The solvent removal required when using other solvents, e.g. by distillation, can be dispensed with here. In this procedure, graft products of the reactants may also arise in a small fraction.

It is also possible to firstly hydrolyze the copolymers containing anhydride groups so that all of the anhydride groups are present as carboxyl groups, and then to carry out the esterification with (D) in accordance with known methods. Preference is given, however, to the procedure described above.

In addition, the copolymers according to the invention are also obtainable by firstly reacting (A) and (D) to give monoethylenically unsaturated mono- or diesters and then copolymerizing these with (B) and (C), the reaction being carried out such that 5 to 80% of the carboxyl groups present in the copolymer according to the invention are in esterified form.

The copolymers according to the invention are advantageously suitable as additive for cleaners, in particular cleaners for hard surfaces, such as dishwashing and household cleaners, and detergents.

The copolymers according to the invention are characterized here in particular by the following advantageous application properties, which render them particularly suitable for use in detergents: they disperse particles of soiling in an excellent manner and thus prevent redeposition of the soiling onto the fabric during washing. They thus prevent graying of the textiles. In addition, they improve the primary detergency both of liquid and of solid detergents. This is true particularly for particulate soilings, but hydrophobic, oil- and grease-containing fabric soilings are also removed more easily. In addition, they can be incorporated into solid and liquid detergent formulations

without problems. In this connection, it should be emphasized that stability and homogeneity of the liquid detergents are not impaired by the copolymers according to the invention. Undesired phase formations and precipitations are not observed even upon prolonged storage.

The invention accordingly also provides detergent formulations which comprise the copolymers according to the invention as additive. The copolymers according to the invention can be used here in the form of the free acids or in partially or completely neutralized form.

Solid detergent formulations according to the invention comprise, in particular, the following components:

(a) 0.05 to 20% by weight of at least one copolymer according to the invention,

(b) 0.5 to 40% by weight of at least one nonionic, anionic and/or cationic surfactant,

(c) 0.5 to 50% by weight of an inorganic builder,

(d) 0 to 10% by weight of an organic cobuilder and

(e) 0 to 60% by weight of other customary ingredients, such as extenders, enzymes, perfume, complexing agents, corrosion inhibitors, bleaches, bleach activators, bleach catalysts, color transfer inhibitors, further graying inhibitors, soil release polyesters, fiber and color protection additives, silicones, dyes, bactericides, dissolution improvers and/or disintegrants,

where the sum of components (a) to (e) is 100% by weight.

The solid detergent formulations according to the invention may be in the form of powders, granules, extrudates or tablets.

Liquid detergent formulations according to the invention preferably have the following composition:

(a) 0.05 to 20% by weight of at least one copolymer according to the invention,

(b) 0.5 to 40% by weight of at least one nonionic, anionic and/or cationic surfactant,

(c) 0 to 20% by weight of an inorganic builder,

(d) 0 to 10% by weight of an organic cobuilder,

(e) 0 to 60% by weight of other customary ingredients, such as sodium carbonate, enzymes, perfume, complexing agents, corrosion inhibitors, bleaches, bleach activators, bleach catalysts, color transfer inhibitors, further graying inhibitors, soil release polyesters, fiber and color protection additives, silicones, dyes, bactericides, organic solvents, solubility promoters, hydrotropes, thickeners and/or alkanolamines and

(f) 0 to 99.45% by weight of water.

Suitable nonionic surfactants (b) are in particular:

- alkoxylated C_8-C_{22}-alcohols, such as fatty alcohol alkoxylates, oxo alcohol alkoxylates and Guerbet alcohol ethoxylates: the alkoxylation can be carried out with ethylene oxide, propylene oxide and/or butylene oxide. Block copolymers or random copolymers may be present. Per mole of alcohol, they usually comprise 2 to 50 mol, preferably 3 to 20 mol, of at least one alkylene oxide. A preferred alkylene oxide is ethylene oxide. The alcohols preferably have 10 to 18 carbon atoms.

- Alkylphenol alkoxylates, in particular alkylphenol ethoxylates, which comprise C_6-C_{14}-alkyl chains and 5 to 30 mol of alkylene oxide/mole.

- Alkyl polyglucosides which comprise C_8-C_{22}-, preferably C_{10}-C_{18}-alkyl chains and usually 1 to 20, preferably 1.1 to 5, glucoside units.

- N-Alkylglucamides, fatty acid amide alkoxylates, fatty acid alkanolamide alkoxylates, and block copolymers of ethylene oxide, propylene oxide and/or butylene oxide.

Suitable anionic surfactants are, for example:

- sulfates of (fatty) alcohols having 8 to 22, preferably 10 to 18, carbon atoms, in particular C_9C_{11}-alcohol sulfates, $C_{12}C_{14}$-alcohol sulfates, C_{12}-C_{18}-alcohol sulfates, lauryl sulfate, cetyl sulfate, myristyl sulfate, palmityl sulfate, stearyl sulfate and tallow fatty alcohol sulfate.

- Sulfated alkoxylated C_8-C_{22}-alcohols (alkyl ether sulfates): compounds of this type are prepared, for example, by firstly alkoxylating a C_8-C_{22}-, preferably a C_{10}-C_{18}-, alcohol, e.g. a fatty alcohol, and then sulfating the alkoxylation product. For the alkoxylation, preference is given to using ethylene oxide.

- Linear C_8-C_{20}-alkylbenzenesulfonates (LAS), preferably linear C_9-C_{13}-alkylbenzenesulfonates and -alkyltoluenesulfonates.

- Alkanesulfonates, in particular C_8-C_{24}-, preferably C_{10}-C_{18}-, alkanesulfonates.

- Soaps, such as the Na and K salts of C_8-C_{24}-carboxylic acids.

The anionic surfactants are added to the detergent preferably in the form of salts. Suitable cations in this connection are, for example, alkali metal ions, such as sodium, potassium and lithium, and ammonium salts, such as hydroxyethylammonium, di(hydroxyethyl)ammonium and tri(hydroxyethyl)ammonium salts.

Particularly suitable cationic surfactants which may be mentioned are:

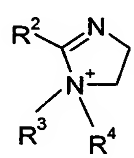
- C_7-C_{25}-alkylamines;

- N,N-dimethyl-N-(hydroxy-C_7-C_{25}-alkyl)ammonium salts;

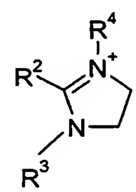
- mono- and di(C_7-C_{25}-alkyl)dimethylammonium compounds quaternized with alkylating agents;

- ester quats, in particular quaternary esterified mono-, di- and trialkanolamines esterified with C_8-C_{22}-carboxylic acids;

- imidazoline quats, in particular 1-alkylimidazolinium salts of the formulae II or III



II



III

in which the variables have the following meanings:

R^2 is C_1-C_{25}-alkyl or C_2-C_{25}-alkenyl;
R^3 is C_1-C_4-alkyl or hydroxy-C_1-C_4-alkyl;
R^4 is C_1-C_4-alkyl, hydroxy-C_1-C_4-alkyl or a radical R^2-(CO)-X-$(CH_2)_p$- (X: -O- or -NH-; p: 2 or 3),

where at least one radical R^2 is C_7-C_{22}-alkyl.

Suitable inorganic builders are, in particular:

- Crystalline and amorphous alumosilicates with ion-exchanging properties, such as, in particular, zeolites: different types of zeolites are suitable, in particular the

zeolites A, X, B, P, MAP and HS in their Na form or in forms in which Na is partially exchanged for other cations such as Li, K, Ca, Mg or ammonium.

- Crystalline silicates, such as, in particular, disilicates and phyllosilicates, e.g. δ- and β-$Na_2Si_2O_5$. The silicates can be used in the form of their alkali metal, alkaline earth metal or ammonium salts, preference being given to the Na, Li and Mg silicates.

- Amorphous silicates, such as sodium metasilicate and amorphous disilicate.

- Carbonates and hydrogencarbonates: these can be used in the form of their alkali metal, alkaline earth metal or ammonium salts. Preference is given to Na, Li and Mg carbonates and hydrogencarbonates, in particular sodium carbonate and/or sodium hydrogencarbonate.

- Polyphosphates, such as pentasodium triphosphate.

Suitable organic cobuilders are, in particular:

- Low molecular weight carboxylic acids, such as citric acid, hydrophobically modified citric acid, e.g. agaric acid, malic acid, tartaric acid, gluconic acid, glutaric acid, succinic acid, imidodisuccinic acid, oxydisuccinic acid, propanetricarboxylic acid, butanetetracarboxylic acid, cyclopentanetetracarboxylic acid, alkyl- and alkenylsuccinic acids and aminopolycarboxylic acids, e.g. nitrilotriacetic acid, β-alaninediacetic acid, ethylenediaminetetraacetic acid, serinediacetic acid, isoserinediacetic acid, N-(2-hydroxyethyl)iminodiacetic acid, ethylenediaminedisuccinic acid and methyl- and ethylglycinediacetic acid.

- Oligomeric and polymeric carboxylic acids, such as homopolymers of acrylic acid and aspartic acid, oligomaleic acids, copolymers of maleic acid with acrylic acid, methacrylic acid or C_2-C_{22}-olefins, e.g. isobutene or long-chain α-olefins, vinyl C_1-C_8-alkyl ethers, vinyl acetate, vinyl propionate, (meth)acrylic esters of C_1-C_8-alcohols and styrene. Preference is given to the homopolymers of acrylic acid and copolymers of acrylic acid with maleic acid. The oligomeric and polymeric carboxylic acids are used in acid form or as the sodium salt.

Suitable bleaches are, for example, adducts of hydrogen peroxide onto inorganic salts, such as sodium perborate monohydrate, sodium perborate tetrahydrate and sodium carbonate perhydrate, and percarboxylic acids, such as phthalimidopercaproic acid.

Suitable bleach activators are, for example, N,N,N',N'-tetraacetylethylenediamine (TAED), sodium p-nonanoyloxybenzenesulfonate and N-methylmorpholinium acetonitrile methylsulfate.

Enzymes preferably used in detergents are proteases, lipases, amylases, cellulases, oxidases and peroxidases.

Suitable color transfer inhibitors are, for example, homopolymers, copolymers and graft polymers of 1-vinylpyrrolidone, 1-vinylimidazole and 4-vinylpyridine N-oxide. Homopolymers and copolymers of 4-vinylpyridine reacted with chloroacetic acid are also suitable as color transfer inhibitors.

Detergent ingredients are otherwise generally known. Detailed descriptions are given, for example, in WO-A-99/06524 and 99/04313; in Liquid Detergents, editor: Kuo-Yann Lai, Surfactant Sci. Ser., Vol. 67, Marcel Decker, New York, 1997, pp. 272-304.

Examples

I. Preparation of copolymers according to the invention

Copolymers 1 to 9

108 g (1.10 mol) of maleic anhydride (A1) were dissolved in x_1 g (x_2 mol) of the alcohol alkoxylate (D) and heated to 90°C under nitrogen and with stirring. At this temperature, 6 g of tert-butyl peroctoate, dissolved in a small partial amount of the alcohol alkoxylate (D), and a solution of y_1 g (y_2 mol) of the monomer (C) in z_1 g (z_2 mol) of styrene were slowly added dropwise over 2 h.

The resulting reaction mixture was then stirred for 4 h at 150°C. The resulting oil was taken up in 500 g of water, and the solution was adjusted to pH 6-7 with sodium hydroxide solution.

30 to 45% strength by weight low-viscosity polymer solutions were obtained. The K values of the copolymers prepared were determined in accordance with H. Fikentscher, Cellulose-Chemie, volume 13, 58-64 and 761-774 (1932) in aqueous solution at 25°C and a polymer concentration of 1% by weight.

Further details relating to these experiments and also the results thereof are summarized in table 1.

The alcohol alkoxylates (D) used were:

D1: methylpolyethylene glycol with an average molecular weight M_n of 500

D2: methylpolyethylene glycol with an average molecular weight M_n of 1 000
D3: ethoxylated $C_{13}C_{15}$-oxo alcohol (7 mol of EO/mol)

Table 1

Copo-lymer	x_1 g (x_2 mol)	D	y_1 g (y_2 mol)	Monomer C	z_1 g (z_2 mol)	K value
1	550 (1.10)	D1	12 (0.14)	acrylic acid	100 (0.96)	36
2	550 (1.10)	D1	11 (0.11)	n-butyl vinyl ether	102 (1.00)	13
3	550 (1.10)	D1	50 (0.12)	allyl alcohol ethoxylate (10 mol of EO/mol)	102 (1.00)	20
4	550 (1.10)	D1	28 (0.28)	methyl methacrylate	86 (0.84)	25
5	550 (1.10)	D1	12 (0.11)	N-vinylpyrrolidone	102 (1.00)	43
6	550 (0.55)	D2	16 (0.22)	acrylic acid	92 (0.90)	51
7	560 (1.10)	D3	16 (0.22)	acrylic acid	92 (0.90)	48
8	550 (1.10)	D1	79 (1.10)	acrylic acid	115 (1.12)	51
9	1100 (1.10)	D2	159 (2.20)	acrylic acid	229 (2.20)	43

Copolymers 10 to 14

a) Preparation of the precursors

a1) Precursor PC1 for copolymers 10 to 12:

194 g (2.11 mol) of maleic anhydride (A1) and 20 g of polyethyl vinyl ether (K value 50, 1% strength by weight in cyclohexane at 25°C in accordance with H. Fikentscher) were dissolved in 900 g of xylene and heated to 140°C under nitrogen and with stirring. At this temperature, a mixture of 220 g (2.16 mol) of styrene and 158 g (2.20 mol) of acrylic acid, and a solution of 4 g of di-tert-butyl peroxide in 36 g of xylene were added in parallel over the course of 4 h.

After after-stirring for one hour at 140°C and cooling to 50°C, the solvent was removed under reduced pressure.

The K value of the polymer present in the form of a white powder was 15.9 (1% strength by weight in cyclohexanone at 25°C).

a2) Precursor PC2 for copolymers 13 and 14:

228 g (2.32 mol) of maleic anhydride (A1) and 20 g of polyethyl vinyl ether (K value 50, 1% strength by weight in cyclohexane at 25°C in accordance with H. Fikentscher) were dissolved in 1 100 g of xylene and heated to 140°C under nitrogen and with stirring. At this temperature, a mixture of 230 g (2.25 mol) of styrene and 1 300 g (18.06 mol) of acrylic acid, and a solution of 12 g of di-tert-butyl peroxide in 140 g of xylene were added in parallel over 4 h.

After after-stirring for one hour at 140°C and cooling to 50°C, the solvent was removed under reduced pressure.

The K value of the polymer present in the form of a white powder was 24.2 (1% strength by weight in cyclohexanone at 25°C).

b) Conversion of the precursors to the copolymers

To prepare the copolymers 10 to 14, in each case a mixture of the precursors PC1 and PC2 and x mol of the alcohol alkoxylate (D) per mole of maleic anhydride were heated to 170°C under nitrogen and with stirring.

After stirring for four hours at 170°C and cooling to 50°C, the resulting oil was dispersed with sodium hydroxide solution. The molar ratio of sodium hydroxide solution to (maleic anhydride + acrylic acid) was 0.6:1.0, giving 30 to 40% strength by weight dispersions of the copolymers with a pH of from 6 to 7.

Further details relating to these experiments and the results thereof are summarized in table 2.

The alcohol alkoxylates (D) used were:

D2: methylpolyethylene glycol with an average molecular weight M_n of 1 000
D3: ethoxylated $C_{13}C_{15}$-oxo alcohol (7 mol of EO/mol)
D4: random butylpolyalkylene glycol copolymer (EO:PO in the weight ratio 1:1) with an average molecular weight M_n of 1 000
D5: $C_{13}C_{15}$-oxo alcohol (5 mol of PO/mol, 5 mol of EO/mol)
D6: $C_{13}C_{15}$-oxo alcohol (12 mol of EO/mol, 3 mol of PO/mol)

Table 2

Copolymer	Precursor	x mol/mol of MAA	Alcohol alkoxylate	K value
10	PC1	0.75	D4	32
11	PC1	0.75	D5	35
12	PC1	1.0	D3	29
13	PC2	1.0	D2	43
14	PC2	1.0	D6	36

II. Use of copolymers according to the invention in detergents

Primary and secondary detergency of the copolymers according to the invention was determined.

For the washing experiments, three solid detergent formulations (DT 1 to 3) and 2 liquid detergent formulations (DT 4 and 5) were used, the composition of which is given in table 3. The washing conditions are listed in table 4.

Table 3

	DT 1	DT 2	DT 3	DT 4	DT 5
Ingredients	[% by wt.]	[% by wt.]	[% by wt.]	[% by wt.]	[% by wt.]
Linear alkylbenzenesulfonate	5.0	0.8	7.0		
C_{12}-C_{18}-alkyl sulfate		12.0		26.7	6.1
C_{12}-fatty alcohol sulfate x 2 EO				7.1	
$C_{13}C_{15}$-oxo alcohol x 7 EO	5.0	4.7	7.0		
$C_{12}C_{14}$-fatty alcohol x 7 EO				6.0	26.0
Soap	1.4	0.4	0.8		
Coconut fatty acid				5.0	14.3
Potassium hydroxide				1.4	5.4
Sodium citrate x $2H_2O$		5.0	10.0	2.1	4.1
Zeolite A	30.0	15.0			
Phyllosilicate SKS 6		14.0			
Sodium carbonate	12.0		20.0		1.4
Sodium hydrogencarbonate		9.0			
Sodium metasilicate x $5H_2O$	3.6				
Sodium disilicate			5.0		
Disodium tetraborate				2.2	
Sodium perborate monohydrate	20.0				

Sodium percarbonate		18.0	15.0		
Tetraacetylethylenediamine	6.0	4.5	4.0		
Methylpropyl glycol				10	
Ethanol					2
Sodium sulfate	7.0	3.2	25.0		
Magnesium silicate		0.8			
Water	ad 100	ad 100	ad 100	ad 100	ad 100

Table 4

Washing conditions	
Device	Launder-o-meter from Atlas, Chicago, USA
Washing liquor	250 ml
Washing time	30 min at 40°C
Detergent concentration	4.5 g/l
Water hardness	3 mmol/l Ca:Mg:HCO_3 4:1:8
Liquor ratio	1:12.5
Washing cycles	1
Copolymer addition	2.5% by weight, based on the respective DT
Test fabric	5.0 g of cotton fabric 221 (bleached, weight per unit area 132 g/m^2)
	5.0 g of blended fabric 768 (65:35 polyester:cotton, bleached, weight per unit area 155 g/m^2)
Soiled fabric	10 g of cotton fabric 290 (twill ware, bleached, weight per unit area 193 g/m^2), soiled with a 1:1:1 mixture of 3 types of clay (Na/Al silicate proportion of the soiled fabric 4.53% by weight)
Types of clay	Niederahr red-burning clay 178/RI Hessian brown-burning manganese clay 262 Yellow-burning clay 158/G all from Jäger KG, Hilgert, Germany

To determine the primary detergency, the degree of whiteness of the soiled fabric was measured before and after washing using a Datacolor photometer (Elrepho® 2000) by reference to the reflectance (%). The higher the reflectance value, the better the primary detergency.

The results obtained are summarized in table 5.

Table 5

Detergent	Copolymer additive (2.5% by weight)	Cotton 290
		Reflectance in %
unwashed		16.3
DT 1	without	21.9
DT 1	Copolymer 4	24.4
DT 1	Copolymer 7	23.8
DT 1	Copolymer 12	25.0
DT 2	without	22.0
DT 2	Copolymer 2	24.0
DT 2	Copolymer 5	24.9
DT 4	without	21.2
DT 4	Copolymer 1	23.0
DT 4	Copolymer 4	23.5
DT 4	Copolymer 7	22.9
DT 5	without	21.3
DT 5	Copolymer 2	22.8
DT 5	Copolymer 4	23.3
DT 5	Copolymer 14	23.9

To determine the secondary detergency, the graying of the white test fabric was measured by determining the degree of whiteness before and after washing using a Datacolor photometer (Elrepho® 2000) by reference to the reflectance (%). The greater the drop in the degree of whiteness, the greater the graying of the fabric, and vice versa.

The results obtained are summarized in table 6.

Table 6

Detergent	Copolymer additive (2.5% by wt.)	Cotton 221	Blended fabric 768
		Reflectance in %	Reflectance in %
unwashed		83.2	84.9
DT 1	without	55.2	55.4
DT 1	Copolymer 1	59.9	60.5
DT 1	Copolymer 4	61.0	61.9
DT 1	Copolymer 5	60.9	61.1
DT 1	Copolymer 6	59.2	61.0
DT 1	Copolymer 8	63.1	61.8
DT 1	Copolymer 9	62.4	61.2
DT 1	Copolymer 12	60.8	61.2
DT 2	without	54.3	55.5
DT 2	Copolymer 1	60.5	60.6
DT 2	Copolymer 2	60.1	59.7
DT 2	Copolymer 3	59.6	61.1
DT 2	Copolymer 10	60.7	60.2
DT 2	Copolymer 11	59.3	58.5
DT 3	without	51.4	52.1
DT 3	Copolymer 1	55.5	54.2
DT 3	Copolymer 8	57.5	58.1
DT 3	Copolymer 13	56.9	56.5
DT 4	without	48.4	54.8
DT 4	Copolymer 1	59.5	60.6
DT 4	Copolymer 4	56.6	59.3
DT 4	Copolymer 5	58.0	60.1
DT 4	Copolymer 6	60.3	58.9
DT 4	Copolymer 8	57.4	57.4
DT 4	Copolymer 9	58.4	56.9
DT 5	without	53.4	46.7
DT 5	Copolymer 2	59.5	54.9
Detergent	Copolymer as additive (2.5% by wt.)	Cotton 221	Blended fabric 768

		Reflectance in %	Reflectance in %
DT 5	Copolymer 4	59.2	58.0
DT 5	Copolymer 5	29.3	55.3

To ascertain the stability of the copolymers in various liquid detergent formulations, in each case 1% by weight of copolymer was formulated into the liquid detergent, and a visual assessment with regard to phase separation, clouding, incompatibilities, etc. was undertaken.

The stability tests were carried out with liquid detergent formulations DT 4 and 5.

Table 7 summarizes the visual assessments after storage for 4 weeks at 40°C.

Table 7

Copolymer	DT 4	DT 5
without	clear	clear
Copolymer 2	clear	clear
Copolymer 3	clear	clear
Copolymer 4	streaks	clear
Copolymer 5	clear	clear
Copolymer 8	clear	clear
Copolymer 9	clear	clear
Copolymer 13	clear	clear